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GEOLOGICAL SCIENCE TECHNIQUES FOR THIN FILM IMPROVEMENT

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LONG-TERM GOALS

First, to characterize and determine the structure-property relationship of complex oxide thin films grown by pulsed laser deposition (PLD). Second, to act as liaison between researchers in the geologic community and the new microanalytical Trace Element Accelerator Mass Spectrometer (TEAMS) laboratory facility being built at NRL.

SCIENTIFIC OBJECTIVES

- 1) To provide precise and accurate compositional analyses of complex oxide thin films to determine if they are stoichiometric and homogeneous laterally, and to provide detailed characterization of their microstructures. The purpose is to determine whether observed unexplained differences in electrical or magnetic properties of thin films relative to bulk materials might be related to compositional or microstructural factors in the thin films. Results will allow workers to grow thin films of improved quality.
- 2) To develop geoscience applications of TEAMS and establish collaborative research projects that can utilize its unique capabilities to address important problems in trace element and isotope geochemistry to advance our understanding of geologic materials and processes.

APPROACH

For compositional analysis of oxide thin films, perform wavelength-dispersive electron microprobe and energy-dispersive SEM measurements, and for detailed microstructural analysis perform SEM. For the TEAMS project, determine geologic applications, establish collaborative projects, and disseminate information on the capabilities of the technique. TEAMS will have the unique combination of extremely high sensitivity (parts-per-trillion detection levels), high spatial resolution (approximately 10 μm), and multi-element analysis, allowing analyses not been previously possible with other techniques.

WORK COMPLETED

Research on the structure-property relationship of ferroelectric thin films was completed.

I investigated the composition and microstructure of rare-earth element substituted lanthanum manganate thin films that display colossal magnetoresistance (CMR). Electron microprobe analyses showed incorrect initial thin film compositions, and allowed a change in deposition approach. I also conducted SEM examinations to determine whether PLD can be used deposit films through patterned shadow masks and concluded that patterned PLD was not as straightforward as originally hoped. Recommendations were made if the project was to be continued.

I coordinated a workshop with Ken Grabowski (NRL) on TEAMS, the purpose of which was to introduce this novel microanalytical technique to potential users and sponsors. The workshop was hosted by NRL,

sponsored by ONR, and consisted of invited talks in a variety of scientific disciplines, as well as focused discussion groups. I coordinated the geoscience portion of the workshop.

I continued researching the possibility of using TEAMS to analyze sea floor gas hydrates and associated marine sediments. I attended a workshop on gas hydrates at NRL. Much research to date has been geophysical. Little geochemistry has been done.

RESULTS

The study of ferroelectric thin films of $\text{Ba}_x\text{Sr}_{(1-x)}\text{TiO}_3$ ($x=0$ and 0.5) grown at a range of temperatures showed stoichiometric SrTiO_3 films, but Ba-deficient $(\text{Ba},\text{Sr})\text{TiO}_3$ films, with average $(\text{Ba}+\text{Sr})/\text{Ti}$ around 0.93 . The thin films display a columnar microstructure; column widths are 50 to 100 nm. Thus, they are fine-grained. Their grain size was not previously known. Other workers noted a strong correlation of grain size with dielectric properties in bulk ferroelectric materials. Decreasing grain size results in lower dielectric constants, broader temperature dependence of the dielectric constant, and reduced Curie temperatures relative to coarse-grained bulk ferroelectrics, exactly the properties observed in the thin films. Thus, the small grain size of the thin films is problematic and can account for the significant differences in dielectric properties. I presented a paper on this research at the Materials Research Society meeting in Boston in December 1996.

IMPACT/APPLICATIONS

My analyses of the chemical and physical composition of ferroelectric thin films showed both compositional and microstructural problems in the thin films that were not previously known.

TRANSITIONS

The problems in the ferroelectric thin films are being addressed by other workers to improve the quality and compositions of the thin films. My SEM examinations showed that annealed films had an improved microstructure, and measurements by others showed improvements in electrical properties of annealed films.

RELATED PROJECTS

This thin film research supported ongoing efforts with SPAWAR and DARPA to implement novel thin film materials produced by pulsed laser deposition into functional devices for the DoD. In addition, this work has generated collaborations between NRL/DC and NRL/Stennis to investigate the dynamics of gas hydrate formation, and their stability.

REFERENCES

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